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62 separate items are enclosed

2303 M2CT ERC # 99-021 ? TP-FY99-Ø122

✓ Spreadsheet
✓ DTS

MEMORANDUM FOR PRS (In-House)

FROM: PROI (TI) (STINFO) 28 May 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-FY99-0122**
Suri and Tinnirello, "Bicyclopropylidene and 1,5-Hexadiyne from Bench Scale to Pilot Scale: Problems and Solutions"

Presentation **HEDM Conference** **(Statement A)**

Bicyclopropylidene and 1,5-Hexadiyne from Bench Scale to Pilot Scale: Problems and Solutions

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Presentation Outline

- Goal
- Criteria for Fuel Selection
- Structural Requirements and Selection for hydrocarbons
- Synthetic Results and Scale Up Challenges
- Future Efforts

Goal

- To come up with a fuel with 2-5% increase of Isp over LOX/RP-1
  - LOX/RP-1(del.) = 263 sec*
  - LOX/RP-1(calc.)= 300 sec*

* *Determined at sea level and 1000 psi chamber pressure*

Task Objective

- Survey of energetic hydrocarbons
- Selection of hydrocarbons based on improved theoretical performance
- Synthesis of target hydrocarbons at bench scale
  - Easy preparation, ~~C~~ lc ost effective and safe
- Translate bench-scale synthesis to pilot scale

Criteria for Fuel Selection

- Predicts Better Performance (Isp) Over LOX/RP-1 System
- Most Desirable Physical Properties
  - Lower Vapor Pressure Compared to RP-1
  - Higher Density (≥ RP-1 = 0.801 g/mL)
  - Freezing Point (≤ -10 °C; RP-1 = -41.4 °C)
  - Boiling Point ≥ B. P. of RP-1
- Thermally Stable
- Compatible with the Current System

Structural Requirement for High Energy Contents

- The Energy Contents Can be Increased by Adding Unsaturation in the Molecule

	$-(CH_2)-$	$CH_2{=}CH_2$	$HC{\equiv}CH$	
$\Delta H_f/C$	~ -5	~ 6.25	~ 27.1	Kcal/mole

Heat of Formation of Saturated Hydrocarbons

- **Compound** **Structure** **ΔH_f (Obs)**
- Ethane CH_3CH_3 -20.04
- Propane $CH_3CH_2CH_3$ -25.02
- Butane $CH_3(CH_2)_2CH_3$ -30.03
- Pentane $CH_3(CH_2)_3CH_3$ -35.08

- $\Delta H_f/C = \sim -5$ ~~K~~kcal/mole

Heat of Formation of Unsaturated Hydrocarbons

- **Compound** **Structure** **ΔH_f(Obs)**
- Ethylene $CH_2{=}CH_2$ +12.5
- 1,3-Butadiene $CH_2{=}CH{-}CH{=}CH_2$ +26.11

  $\Delta H_f/C = \sim +6.25$ lc ~~K~~cal/mole

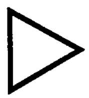
- Acetylene $HC{\equiv}CH$ +54.36

  $\Delta H_f/C = \sim + 27.1$ lc ~~K~~cal/mole

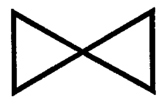
Structural Requirement for High Energy Contents (Cont….)

- The Energy Contents is Also Increased by Incorporating Strain in the Molecule
  - Ring Compound — ΔH_f
  - Cyclopropane — + 12.73 Kcal/mole
  - Cyclobutane — + 6.78 Kcal/mole
  - Cyclopentane — - 18.44 Kcal/mole

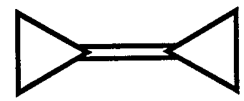
Survey of Hydrocarbons



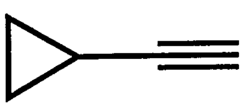
Cyclopropane
ΔHf = 12.7 Kcal/mole
= 0.3 Kcal/g
Isp = 312 Sec.



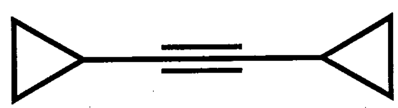
[2.2] Spiropentane
ΔHf = 44.4 Kcal/mole
= 0.65 Kcal/g
Isp = 311 Sec.



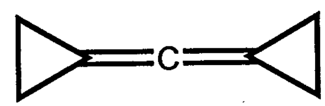
Bicyclopropylidene
ΔHf = 76.1 Kcal/mole
= 0.95 Kcal/g
Isp = 312.5 Sec.



Cyclopropylacetylene
ΔHf = 64.0 Kcal/mole
= 0.97 Kcal/g
Isp = 311.3 Sec.

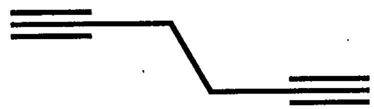


Bicyclopropylacetylene
ΔHf = 73.4 Kcal/mole
= 0.69 Kcal/g
Isp = 307.2 Sec.

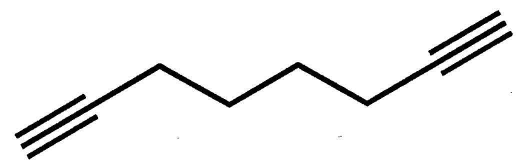


Dicyclopropylidenemethane
ΔHf = 104.6 Kcal/mole
= 1.13 Kcal/g
Isp = 313.4 Sec.

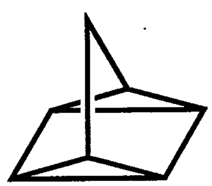
Survey of Hydrocarbons



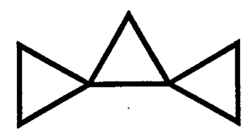
1,5-Hexadiyne
ΔH_f = 91.8 ~~K~~cal/mole
= 1.18 ~~K~~cal/g
I_{sp} = 311.8 ~~S~~ec



1,7-Octadiyne
ΔH_f = 79.9 ~~K~~cal/mole
= 0.75 ~~K~~cal/g
I_{sp} = 308.2 ~~S~~ec



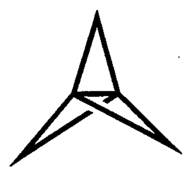
Quadricyclane
ΔH_f = 72.2 ~~K~~cal/mole
= 0.78 ~~K~~cal/g
I_{sp} = 307 ~~S~~ec



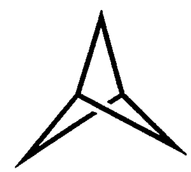
[3]–Triangulane
ΔH_f = 72.3 ~~K~~cal/mole
= 0.77 ~~K~~cal/g
I_{sp} = 311.4 sec

Survey of Hydrocarbons

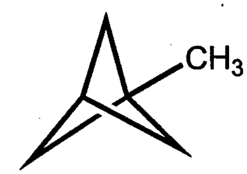
[1.1.1]Propellane and its Derivatives



ΔHf = 83.0 ~~K~~cal/mole
= 1.25 ~~K~~cal/g
Isp = 316.6 sec

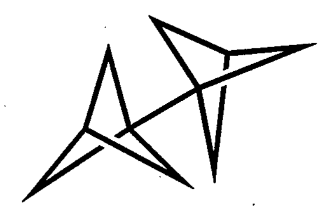


ΔHf = 51.0 ~~K~~cal/mole
= 0.75 ~~K~~cal/g
Isp = 313.9 sec



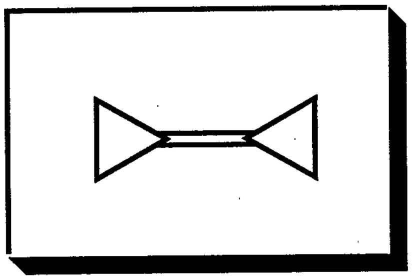
ΔHf = 45.0 ~~K~~cal/mole
= 0.54 ~~K~~cal/g
Isp = 311.2 sec

ΔHf = 26.0 ~~K~~cal/mole
= 0.21 ~~K~~cal/g
Isp = 308.0 sec



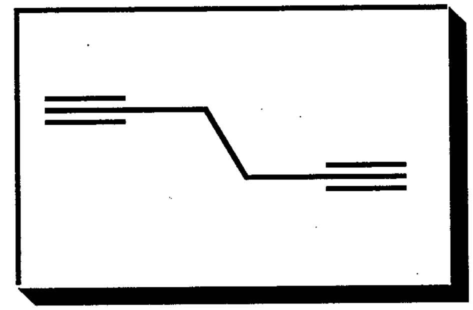
ΔHf = 95.0 ~~K~~cal/mole
= 0.70 ~~K~~cal/g
Isp = 309.9 sec

Selection of Target Molecules



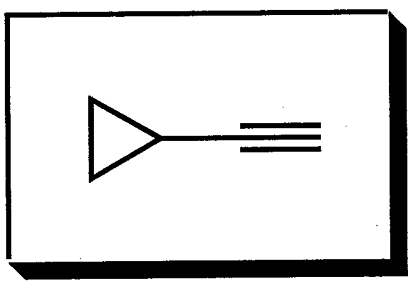
Bicyclopropylidene

$I_{sp} = 312.5$ ~~S~~ec



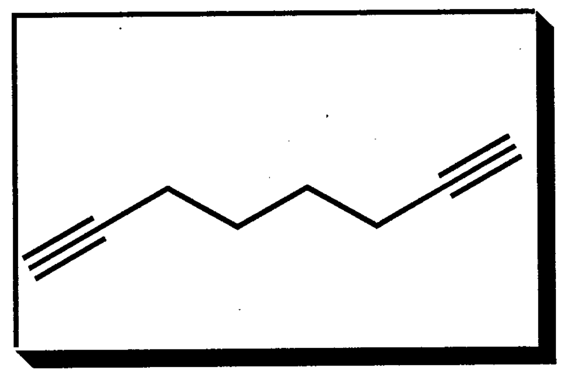
1,5-Hexadiyne

$I_{sp} = 311.8$ ~~S~~ec



Cyclopropylacetylene

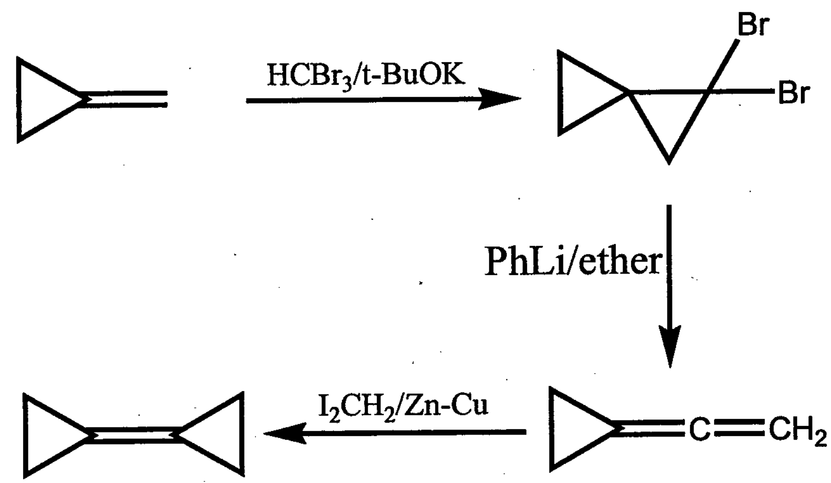
$I_{sp} = 311.3$ ~~S~~ec



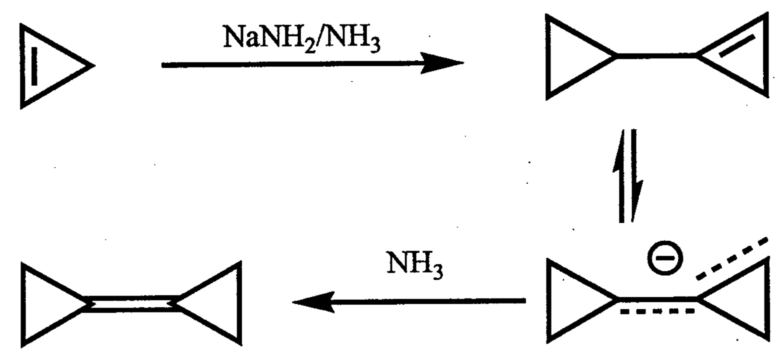
1,7-Octadiyne

$I_{sp} = 308.2$ ~~S~~ec

Literature Methodology

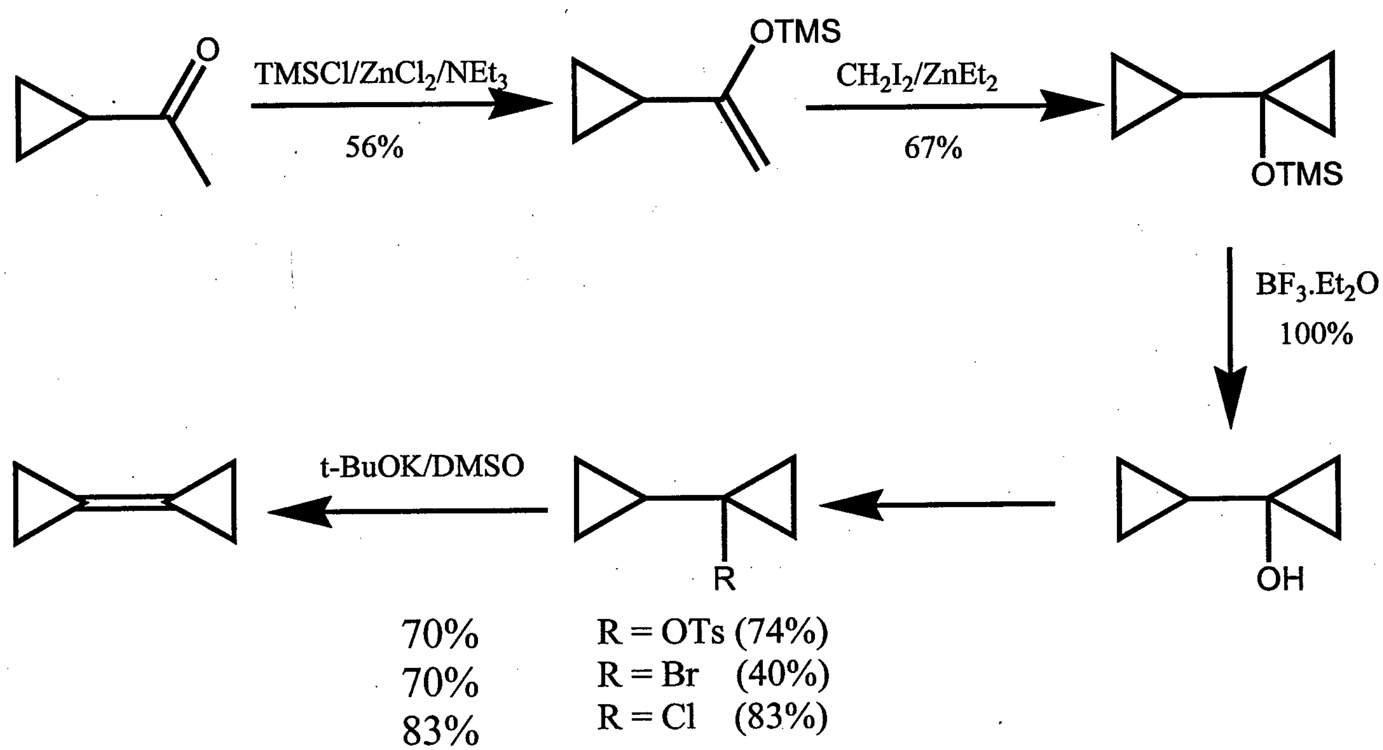


P. LePerchec and J. M. Conia, *Tetrahedron Lett.* **1970**, 1587



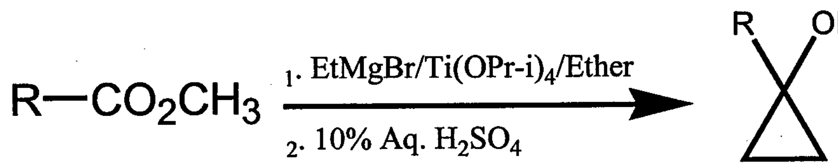
A.J. Schipperojn, *Rec. Trav. Chim. Pays-Bas* **1971**, 90, 1110

Literature Methodology

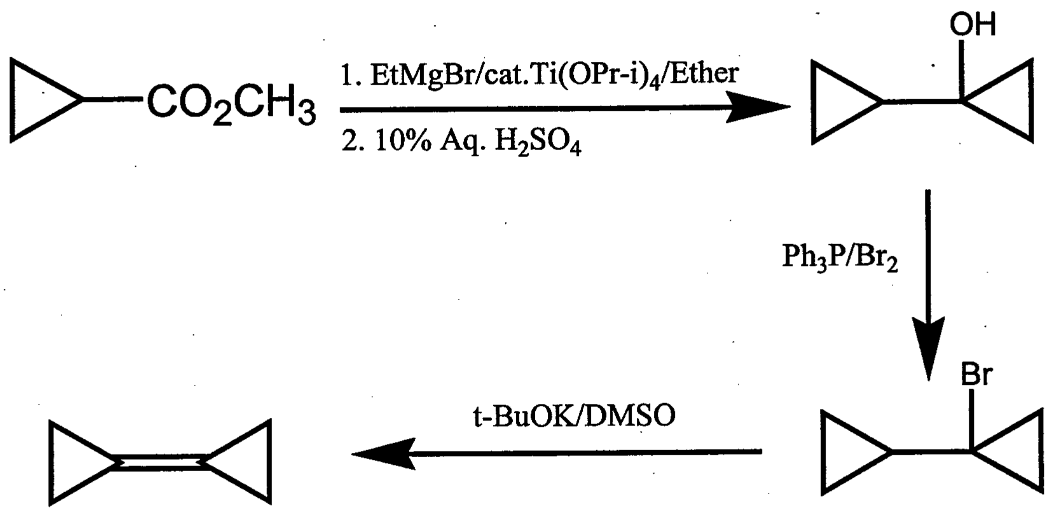


1. A.H. Schmidt, U. Schirmer and J.-M. Conia; *Chem. Ber.* **1976**, 109, 258
2. W. Weber and A.de Meijere; *Syn. Comm.* **1986**, 16, 837

Kulinkovich Reaction

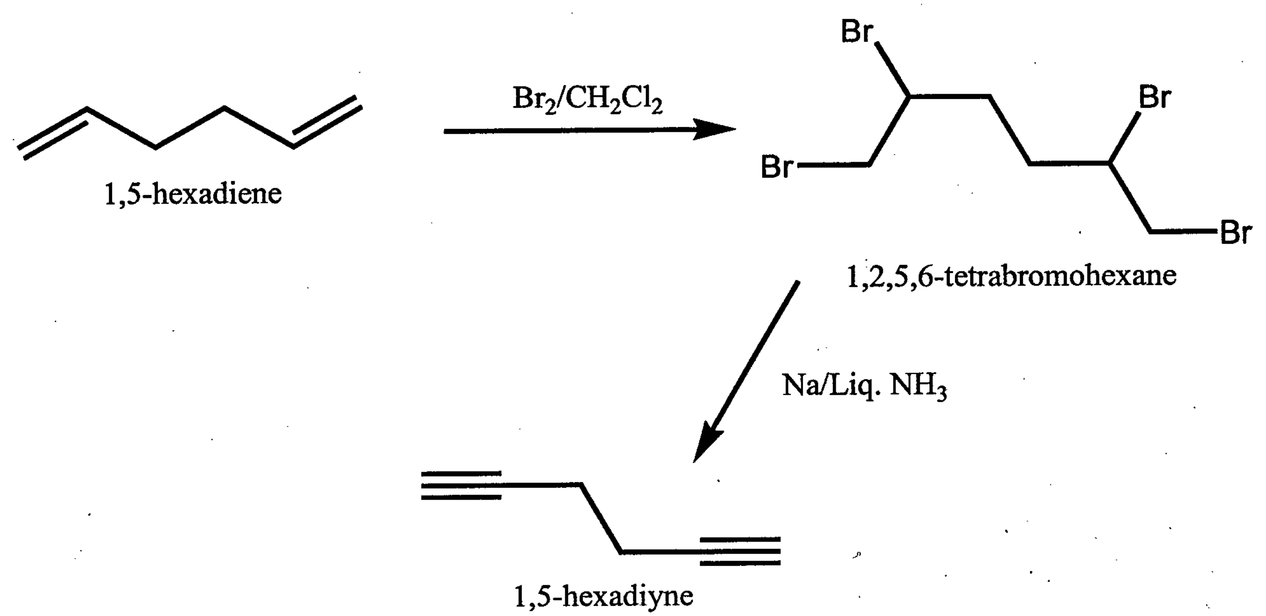


O. G. Kulinkovich, S. V. Sviridov, D. A. Vasilevskii; *Synthesis* **1991**, 234



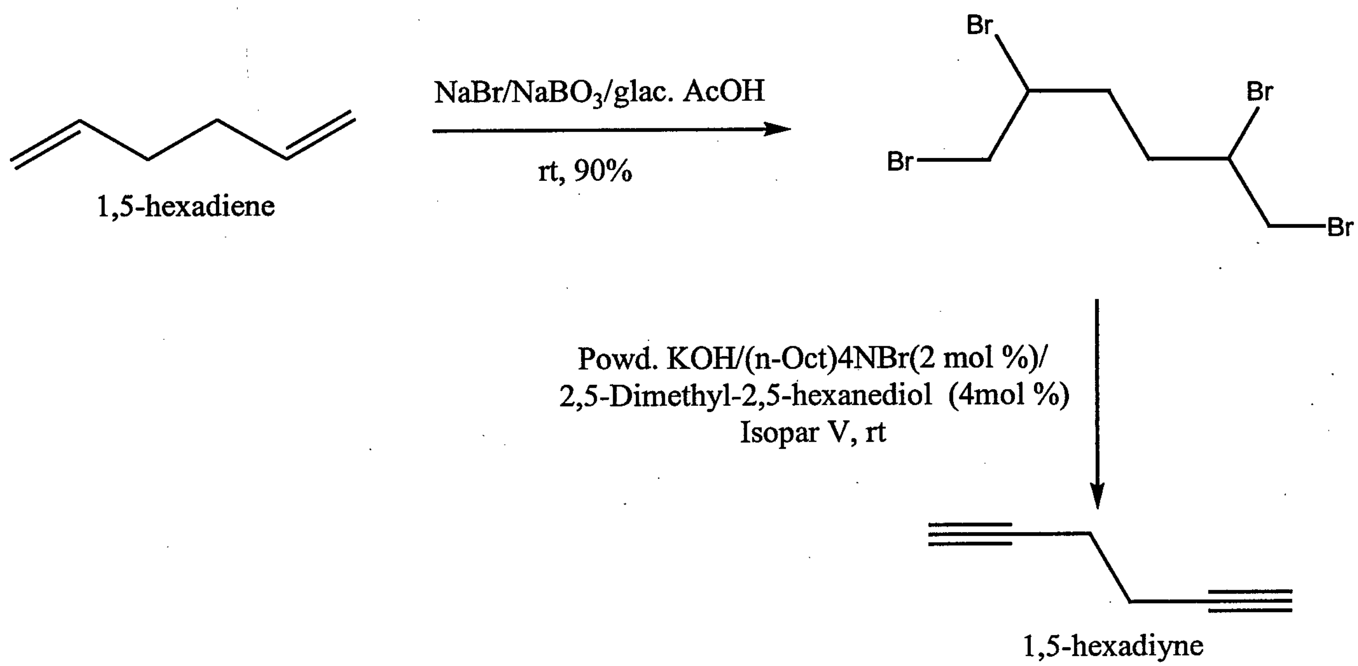
1. A.de Meijere, S. I. Kozhushkov, T. Spaeth and N. S. Zefirov; *J. Org. Chem.* **1993**, 58, 502
2. S.C. Suri; *Technical Report PL-TR-97-3057*, **1997**, p 26

Literature Methodology for 1,5-Hexadiyne



AFRL/PRS Methodology

- Eliminated Use of Free Halogen
- Eliminated Use of Methylene Chloride
- Eliminated Use of Liquid Ammonia/Sodium

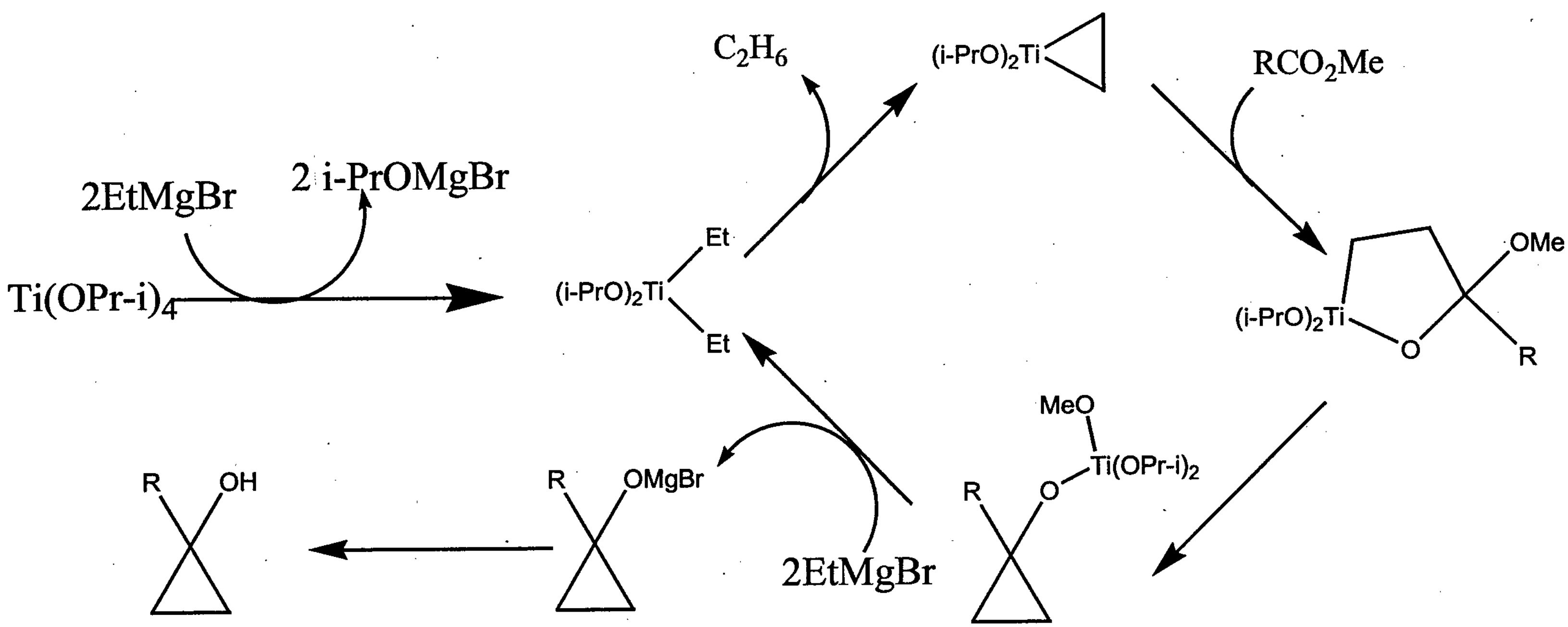

NaBr/NaBO$_3$/glac. AcOH
rt, 90%
1,5-hexadiene
Br
Br
Br
Br
Powd. KOH/(n-Oct)4NBr(2 mol %)/
2,5-Dimethyl-2,5-hexanediol (4mol %)
Isopar V, rt
1,5-hexadiyne

Hazard Characteristics of Hydrocarbons

Compound	Olin Matheson Liquid Impact*	Julius Peters Sliding Friction*	NOL Card GAP At Zero Card
RP-1	>200 ~~K~~g/~~C~~m lc lc	>371N	Negative
Bicyclopropylidene	>200 ~~K~~g/~~C~~m lc lc	133N	Negative
Cyclopropylacetylene	>200 ~~K~~g/~~C~~m lc lc	78N	Negative
1,5-Hexadiyne	56 ~~K~~g/~~C~~m lc lc	112N	Negative
1,7-Octadiyne	148 ~~K~~g/~~C~~m lc lc	100N	Negative

* Obtained five negative results

Proposed Mechanism of Kulinkovich Reaction



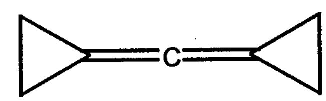
Problems	Consequences	Solution
• Rise in temperature (Exothermic reaction)	• Loss of flammable solvent (F_p=-45 °C) • Product rearranges to cyclopropyl ethyl ketone	• Perform addition of Grignard reagent below 0 °C • Operation is done below 30 °C
• Water contamination	• Decreases the concentration of Grignard reagent	• Purge the reactor with nitrogen gas all the time to reduce the condensation of water vapors in the reactor. • Use anhydrous ether
• High acid concentration while quenching	• Probability of formation of rearranged product	• Use of low concentration of acid
• Gummy deposit on the wall of reactor and around cooling coil	• Methylcyclopropyl carboxylate entraps in the gummy material.	• Decrease the size of the batch. • Try Continuous Process
• By Products (Isopropanol and Methanol)	• Reacts with brominating reagent in the second step.	• Azetrope removal of Isopropanol & methanol using ethylacetate at ≤ 50 °C

Problems	Consequences	Solution
Contamination of Isopropanol/methanol	Consumption of brominating agent to form 2-bromopropane/ bromomethane	Try to minimize IPA/methanol contamination in step 1. After checking GC, compensate for IPA/Methanol by adding excess of reagent
Contamination of Pyridine	Carried over to next step	Wash the product in pmethylene chloride with aqueous HCl
Distill off solvent directly from reactor	Resulted in thick solid triphenyl phosphine oxide in the reactor.	Transfer to rotary evaporator directly and remove 2/3 of dichloromethane followed by treatment with pentane to form free flowing solid

Problems	Consequences	Solution
• Exothermic Reaction	• Loss of Product	• Reaction vessel is equipped with condensor hooked to chiller at ≤ -10 °C.
• Direct Distillation under high vacuum at room temperature	• Loss of Product	• Quenching by adding the reaction mixture into ice-water and extracted with pentane • Distilling off pentane under vacuum using water aspirator at dry ice-acetone temperature. • Putting multiple cold-traps in series
• Purification	•	• Using packed column • It further removes traces of pentane

Future Target Molecules

Bicyclopropylacetylene
Isp = 307.2 Sec



Bicyclopropylidenemethane
Isp = 313.4

Summary

- The synthesis of 1-cyclopropylcyclopropan-1-ol was developed by generating Grignard reagent in situ, thus avoiding handling of moisture sensitive and flammable preformed ethylmagnesium bromide.
- Three steps synthesis was used to prepare 7-8 lbs of bicyclopropylidene. There is a need to find an alternative synthetic route (maximum 2 steps) for it.
- About 200 g of 1,5-hexadiyne was synthesized using environmentally friendly process that eliminates the use of free bromine, controlled solvent dichloromethane and liquid ammonia, was worked out.
- Collected hazard data on bicyclopropylidene and 1,5-hexadiyne